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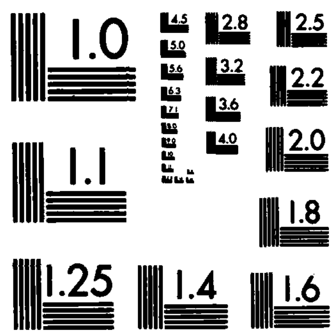

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Rate Constant of the $OH + H_2O_2 \rightarrow HO_2 + H_2O$ Reaction

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Absolute rate constants for the reaction $OH + H_2O_2 \rightarrow HO_2 + H_2O$ have been measured using the flash photolysis resonance fluorescence technique over the temperature range 241 to 413 K and at 1 atm helium. H_2O_2 concentrations were measured by ultraviolet and infrared absorption spectrophotometry. The rate constant at 294 K was found to be $\cancel{K_1} = 1.8 \cancel{\pm} 0.3 \times \cancel{10}^{-12}$ ~~cm~~^{3} ~~molecule~~$^{-1}$ s^{-1}, in agreement with recent literature values. The results yield a curved Arrhenius plot, with a slight increase in the rate constant at the lower temperatures.

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ABSTRACT

Absolute rate constants for the reaction $OH + H_2O_2 \rightarrow HO_2 + H_2O$ have been measured using the flash photolysis resonance fluorescence technique over the temperature range 241 to 413 K and at 1 atm helium. H_2O_2 concentrations were measured by ultraviolet and infrared absorption spectrophotometry. The rate constant at 294 K was found to be $k_1 = 1.8 \pm 0.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, in agreement with recent literature values. The results yield a curved Arrhenius plot, with a slight increase in the rate constant at the lower temperatures.

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INTRODUCTION

The gas phase reaction of OH with H_2O_2 is an important component of the atmospheric HO_x cycle:

$$OH + H_2O_2 \rightarrow HO_2 + H_2O \tag{1}$$

H_2O_2 is formed in the atmosphere mainly by the recombination reaction of HO_2 radicals (reaction 2) and its principal loss processes are reaction with OH radicals (reaction 1) and photodissociation (reaction 3):

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{2}$$

$$H_2O_2 + h\nu \rightarrow OH + OH \tag{3}$$

In addition, rainout and washout processes represent significant sinks for H_2O_2 in the troposphere.

Several previous studies of reaction (1) have been reported: early measurements of the rate constant using steady state photolysis methods (Gorse and Volman, 1972; Meagher and Heicklen, 1979), flash photolysis (Greiner, 1968; Harris and Pitts, 1979), and discharge flow techniques (Hack et al., 1975) gave results in the 0.62-1.2 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1} range at 298 K. More recently, four measurements by two different methods -- discharge flow (Sridharan et al., 1980; Keyser, 1980) and flash photolysis resonance fluorescence (Wine et al., 1982; Kurylo et al., 1982)

-- yielded rate constants that are about a factor of two larger at 298 K and which showed linear Arrhenius plots, with the rate constant decreasing by ~ 10% at 250 K. In this work we essentially confirm these new rate constant values using the flash photolysis resonance fluorescence technique at 1 atm He; however, we observe a curved Arrhenius plot, with the rate constant increasing below room temperature and becoming 10% larger at 250 K.

EXPERIMENTAL

Instrumentation and Chemicals

An all-pyrex jacketed reaction cell with an internal volume of ~ 150 cm^3 was used in the experiments. The cell was maintained at constant temperature by flowing a thermostated liquid through the outer jacket surrounding the cell. The temperature was monitored at five different positions on the cell with copper-constantan thermocouples.

OH radicals were produced by flash photolysis of H_2O_2, HNO_3 and/or H_2O using a nitrogen flash-lamp equipped with a Suprasil quartz lens and operated around 15 kV. An adjustable iris was placed in front of the lens to control the amount of photolysis light reaching the cell, which was unfocused. An OH microwave-discharge lamp excited resonance fluorescence in the 0-0 band of the $A^2\Sigma^+-X^2\Pi$ system ($\lambda \sim 308$ nm). This fluorescence was monitored perpendicular to both the flash lamp and the resonance lamp radiation flux by an EMI-9782QA photomultiplier fitted with an interference filter (290-320 nm, 20% T at 307 nm) and a Corning 7-54 filter. The resonance lamp and the photomultiplier were also fitted with quartz lenses which mildly focused the radiation.

The signals, in the form of photon counts, were processed by a signal averager-computer system (Inotech Ultima II, Data General-Nova 3) using a non-linear least-squares routine to analyze the decays. For each decay rate sufficient flashes (usually 400) were averaged to obtain a well-defined temporal profile of OH concentration over at least 3 1/e times. The residuals and the autocorrelation coefficients were plotted routinely; in no case was there statistical evidence for departures from the single exponential decay expected for pseudo-first order conditions.

In order to avoid accumulation of products and to minimize the decomposition of H_2O_2, the reactant mixture was flowed through the reaction cell with a linear velocity of about 8 cm s^{-1}. The flash lamp repetition rate was about 1 Hz, so that the cell was refilled with a fresh reactant mixture for every flash.

H_2O_2 was introduced into the system by passing He gas through a glass bubbler containing several milliliters of concentrated H_2O_2 solution at 0^oC. For some runs HNO_3 was added in small amounts (5-10 mtorr) in order to provide an alternate more efficient photolytic OH source. A separate bubbler was assembled containing several milliliters of aqueous HNO_3 at 0^oC. Helium gas was slowly bubbled through the liquid and the mixture was added to the H_2O_2/He flow downstream from the UV spectrophotometer. All connections and tubing after the bubblers were either glass or teflon.

Helium gas (Matheson Gas Products) was passed through a molecular sieve trap kept at liquid nitrogen temperature. Hydrogen peroxide (90%, FMC Corporation) was used without further purification. Nitric acid (70%, Mallinckrodt, Analytical Reagent grade) and C_2H_6 (Matheson Gas Products, CP grade) were also used without further purification.

The flow rates were measured using Matheson mass flow meters. Pressures were monitored with an MKS capacitance manometer (0-100 torr range) and with a Bourdon-type Wallace-Tiernan gauge (0-800 torr range).

H_2O_2 Concentration Determination

The H_2O_2 concentrations were measured using a Perkin-Elmer 552 UV-vis spectrophotometer equipped with a 50 cm cell with folded optics, to give an optical path length of 100 cm. Due to the low partial pressures of H_2O_2 used (0.8-13 mtorr), this UV measurement was made before the final dilution with He. The absorbance of the room temperature gas mixture was monitored in the 205-220 nm range, and the concentrations were calculated using the absorption cross section data of Molina and Molina (1981).

For most of the runs, the H_2O_2 concentrations were also measured after the reaction cell by using a Nicolet-7199 Fourier-transform infrared spectrometer (FTIR) equipped with a standard Nicolet data-handling system and a liquid nitrogen cooled HgCdTe detector. A 55 cm long teflon-coated absorption cell with a ~ 6 cm^2 cross section and maintained at room temperature was interfaced to the FTIR. The cell was fitted with internal mirrors and KCl windows, with an optical path of ~ 20 m. The HNO_3 concentrations were also monitored with the FTIR cell. The IR band strengths for H_2O_2 and HNO_3 were calibrated as described earlier (Molina and Molina, 1981).

The H_2O_2 concentrations calculated from UV and IR measurements agreed to within a few percent, except at the highest temperature (413 K), where the discrepancy indicated about 15% decomposition in the resonance fluorescence cell.

Sensitivity and Control Experiments

The OH detection sensitivity of the resonance fluorescence system was calibrated by photolyzing HNO_3/He mixtures at 222 nm with a KrCl excimer laser whose power was measured with a thermopile: at 1 atm He, this sensitivity was $\sim 2 \times 10^{-8}$ counts cm^3 $molecule^{-1}s^{-1}$. Using this figure, the initial OH concentration for the flash photolysis runs was estimated to be at most 10^{12} molecule cm^{-3}.

Some control experiments were carried out to determine the OH + C_2H_6 rate constant in our apparatus, as a function of temperature, using HNO_3 as an OH photolytic source,and using a C_2H_6/He mixture analyzed by gas chromatography. The observed rate constant decreased by a factor of two between 298 K and 250 K, and the results agreed to within 10% at these two temperatures with the values recommended by the NASA Panel for Data Evaluation (DeMore et al., 1982).

RESULTS AND DISCUSSION

Chemical Kinetics

The OH + H_2O_2 reaction was studied over the temperature range 241-413 K and at a He pressure of 760 torr. A total of twenty-five bimolecular rate constants were measured. The results are shown in Table 1.

All experiments were carried out under pseudo-first order conditions:

$$\ln\{[OH]_o/[OH]_t\} = (k_1[H_2O_2] + k_d)t \equiv k^I \cdot t$$

where k_d is the first order rate constant for loss of OH in the absence of H_2O_2 and k^I is the pseudo-first order rate constant. k_1 was obtained from the slope of plots of k^I vs. $[H_2O_2]$. A typical OH decay is shown in Figure 1, and Figure 2 shows a typical plot of k^I vs. $[H_2O_2]$. The individual rate constants were determined from a linear least squares analysis of these latter plots. The value of the intercept agreed well with the value for k_d obtained in the absence of H_2O_2 (with H_2O as the photolytic source of OH). The uncertainties listed in Table 1 represent one standard deviation, that is, about $\pm 3\%$ at 294 K. We estimate that systematic errors raise the uncertainty to $\pm$ 15-20% yielding

$$k_1\ (294\ K) = (1.8 \pm 0.3) \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}.$$

Table 1. Rate Constant Data for the Reaction of OH with H_2O_2

Temperature (K)	Pressure Range H_2O_2 (mtorr)	Pressure HNO_3 (mtorr)	Number of Runs	$k_1 \pm 1\sigma$ (10^{-12} $cm^3 molecule^{-1} s^{-1}$)
241	1.3–6.8	0	13	2.10 ± 0.13
241	2.4–6.0	5	19	2.04 ± 0.07
			Average:	2.07 ± 0.10
251	0.7–5.6	0	12	1.95 ± 0.06
251	0.9–9.7	0	10	1.90 ± 0.05
251	0.9–7.9	0	15	1.90 ± 0.05
			Average:	1.92 ± 0.05
294	1.1–11.3	0	15	1.88 ± 0.11
294	1.8–7.1	0	22	1.86 ± 0.10
294	1.9–6.3	5	12	1.81 ± 0.06
294	1.2–12.0	0	11	1.85 ± 0.04
294	5.0–8.7	0	4	1.71 ± 0.03
294	1.7–9.9	0	7	1.81 ± 0.04
294	1.3–11.0	0	6	1.66 ± 0.05
294	1.3–10.6	0	6	1.81 ± 0.05
294	2.4–8.2	0	4	1.77 ± 0.05
			Average:	1.80 ± 0.06
333	2.4–11.8	0	21	1.66 ± 0.08
333	1.1–9.4	0	12	1.76 ± 0.08
333	0.8–8.3	0	9	1.75 ± 0.04
			Average:	1.72 ± 0.07
365	2.9–9.2	5	17	1.76 ± 0.13
365	2.4–9.8	5	12	1.79 ± 0.15
			Average:	1.78 ± 0.14
413	2.8–6.8	5	9	2.04 ± 0.30
413	2.9–9.2	10	9	1.64 ± 0.12
			Average:	1.84 ± 0.21

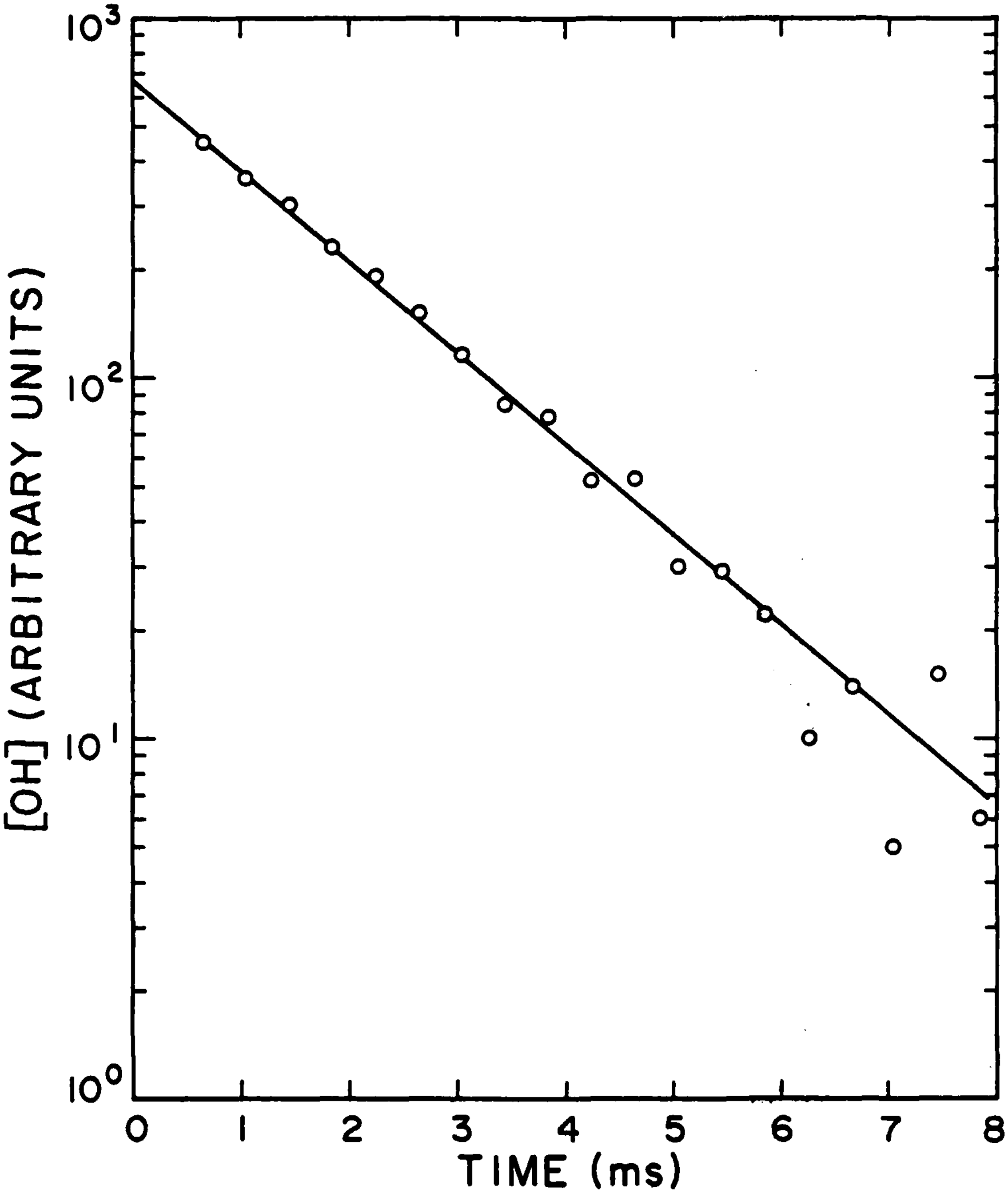


FIGURE 1. Typical OH Temporal Profile following Photolysis of an $H_2O_2/HNO_3/H_2O/He$ Mixture. T = 241 K; P = 760 torr; $[H_2O_2]$ = 5.3 mtorr; $[HNO_3]$ = 4.4 mtorr.

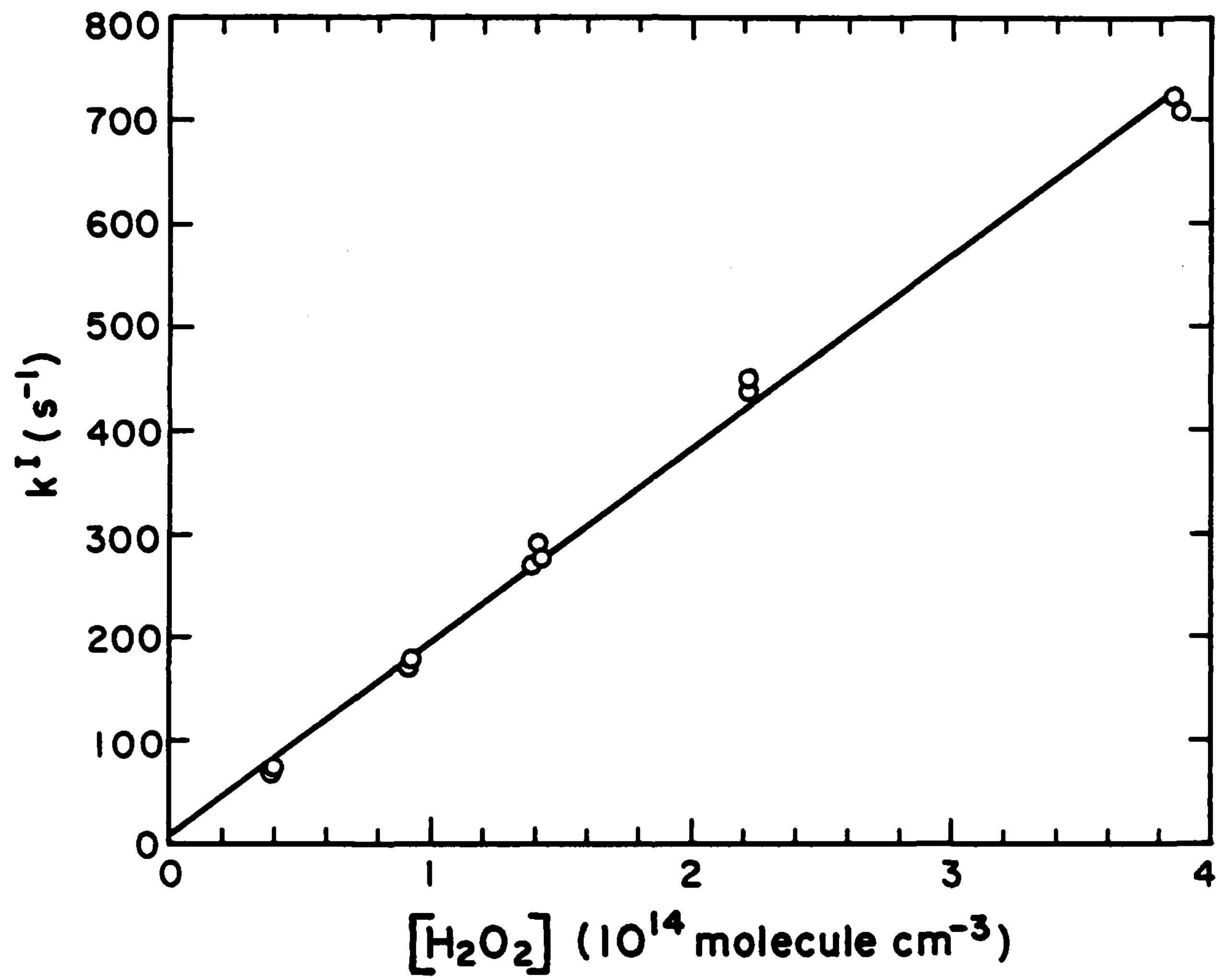


FIGURE 2. Plot of k^I versus $[H_2O_2]$ at Room Temperature and Atmospheric Pressure (first 294 K entry in Table 1). Line is least squares fit of the experimental points.

For runs containing HNO_3, contributions to the observed k^I from the reaction OH + HNO_3 were subtracted out using a rate constant obtained from the Arrhenius Equation $k = 9.4 \times 10^{15}$ exp (778/T0 cm^3 $molecule^{-1}$ s^{-1}, taken from the recommendation of the NASA Panel for Data Evaluation (DeMore et al., 1982). This correction amounted in all cases to less than 10% of the observed pseudo first order rate constant. The addition of HNO_3 provided about a three-fold increase in the signal to noise ratio for an equivalent number of flashes.

Secondary Reactions

Given the relatively small radical concentration ($[OH]_o <$ 10^{12} cm^{-3}) complications from secondary reactions should be minimal. As a check, the initial [OH] was varied by more than a factor of two by changing the intensity of the photolysis light; no significant change was observed in k^I. Also, as may be seen in Table I, the addition of HNO_3 yielded essentially the same results. Furthermore, no departures from an exponential decay in OH were evident in any of the experiments.

The fast reaction between H-atoms and HO_2 radicals is potentially a source of error since OH radicals can be regenerated by this route:

$$H + HO_2 \rightarrow OH + OH \qquad (4)$$

Some H-atoms might have been produced by the flash photolysis of water vapor present in our sample in spite of the 165 nm Suprasil cutoff, but the expected amounts were too small to significantly perturb the OH concentrations: we estimate $[H]_o/[OH]_o < 0.3$ for typical runs without HNO_3 added, and $[H]_o/[OH]_o < 0.1$ in the presence of HNO_3. Computer simulations of the kinetics incorporating reaction 4 as well as other potentially interferring secondary reactions confirmed that under our experimental conditions there should have been no significant departures from the simple exponential decay resulting from the OH + H_2O_2 reaction. The results of these simulations essentially duplicate those presented by Kurylo et al., (1982), and hence they will not be repeated here.

Temperature Dependence

The temperature dependence of the rate constant for the reaction under study is shown in Figure 3, and also in Figure 4 along with the results of the four groups which have studied this reaction recently.

A linear least-squares fit to our results yields the expression:

$$k = (1.47 \pm 0.20) \times 10^{-12} \exp[(70 \pm 41)/T] \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (5)$$

where the uncertainty represents one standard deviation. However, a clear departure from simple Arrhenius behavior is apparent in the figure, and the results are better fitted by the expression

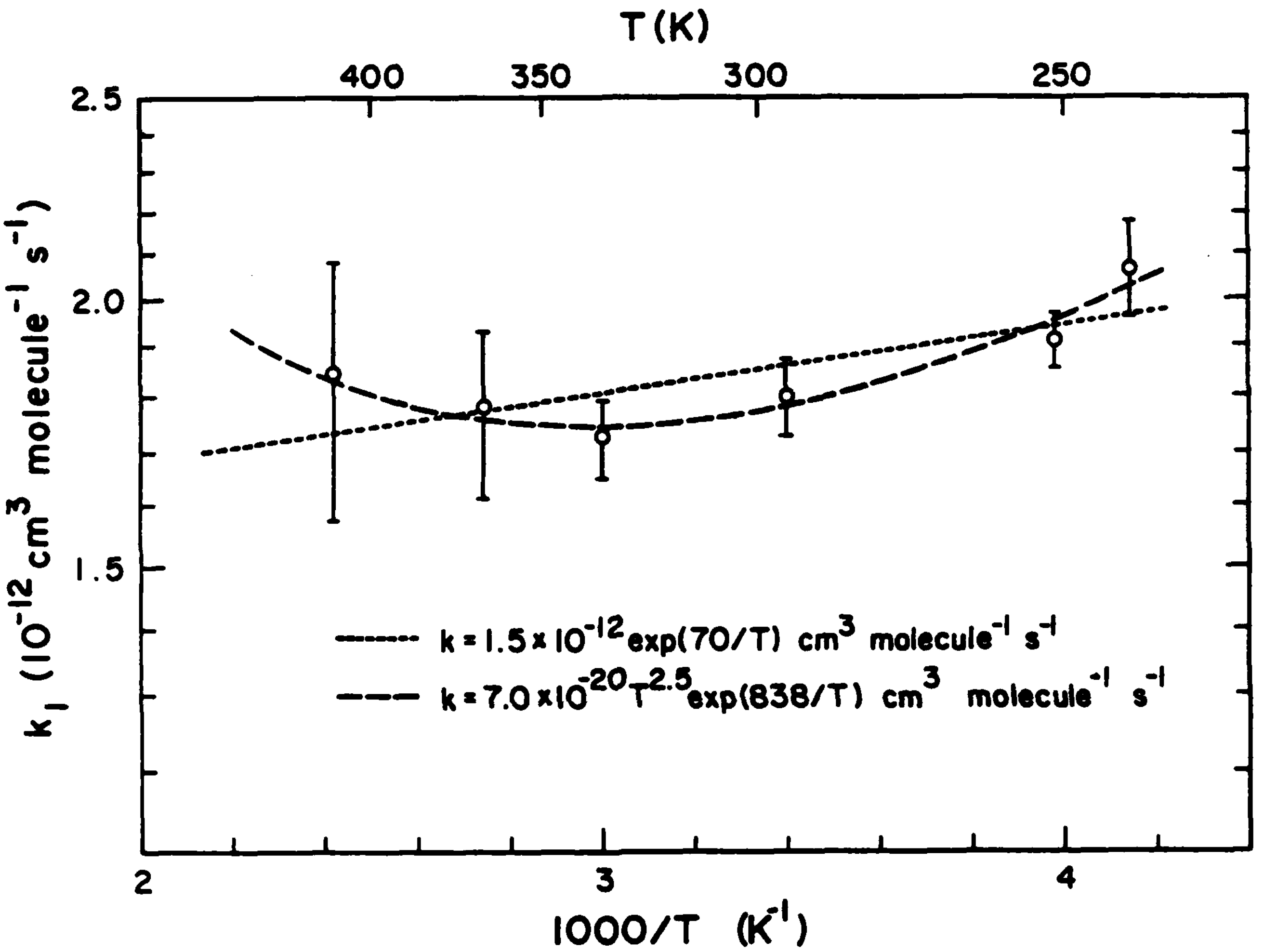


FIGURE 3. Arrhenius Plot from present work: ln (k_1) versus 1/T.

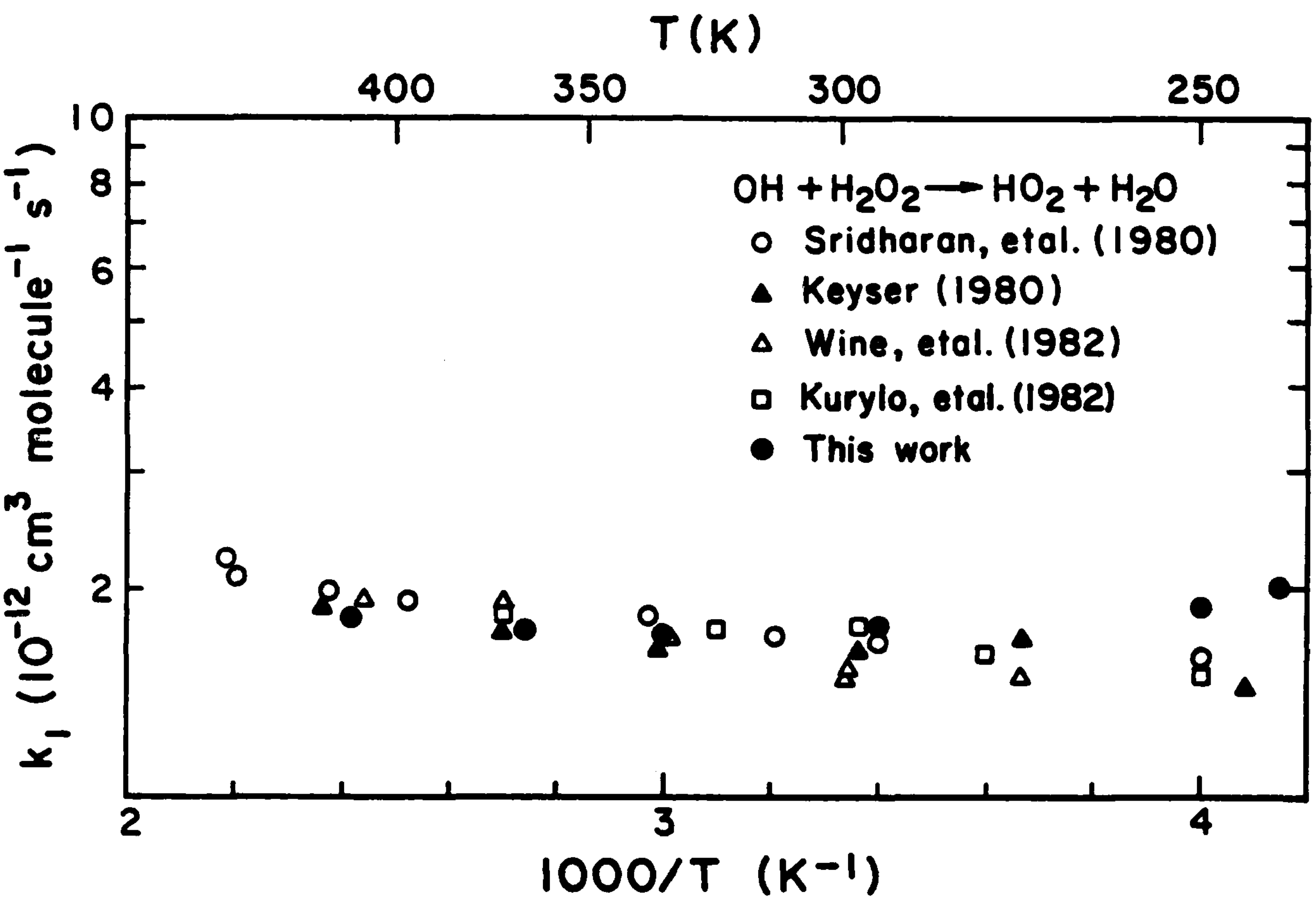
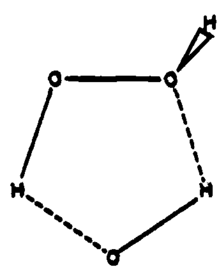


FIGURE 4. Arrhenius Plot of k_1 values from the most recent studies.

$$k = (7.0 \pm 2.0) \times 10^{-20} T^{2.5} \exp[838 \pm 86)/T] \ cm^3 \ molecule^{-1} \ s^{-1} \quad (6)$$

As expected, the fit is insensitive to the exact value of the power n to which T is raised (the minimum standard deviation was actually obtained for n = 2.8). Equation 5 reproduces the experimental rate constant values to within 7%, and equation 6 to within 3%.

Curvature in the Arrhenius plot can be rationalized by assuming the existence of two different reaction mechanisms: a direct H-atom abstraction predominating at the higher temperatures, and an addition mechanism, i.e., a "complex-mode" bimolecular reaction (see, for example, DeMore et al., 1982), predominating at the lower temperatures. Recently Leu and Smith (1982) found similar, even more pronounced curvature in the Arrhenius plot for the reaction OH + H_2S, which they also interpreted in terms of the dual-mechanism postulate. Thus, it appears that at low temperatures the complex-mode mechanism is quite prevalent for reactions of the OH radical with polar molecules which may form hydrogen bonds, e.g., HNO_3, HNO_4, H_2S and H_2O_2, a mechanism which is evidenced by the negative activation energies observed in these reactions (DeMore et al., 1982). The H_2O_2 molecule is nonplanar; a plausible structure for the intermediate adduct is a hydrogen-bonded five—membered ring:



Comparison with Other Measurements

Inspection of Table 2 and Figure 4 shows that our measured rate constants for the OH + H_2O_2 reaction at 273 K and above are in very good agreement with those reported most recently (Sridharan et al., 1980; Keyser, 1980; Wine et al., 1982; Kurylo et al., 1982), but are larger by about 25% at 250 K. The discrepancy appears to lie just within the combined error limits. Sridharan et al. suggested a possible leveling off at the low temperature end of their Arrhenius plot, a trend which appears also in the data of Wine et al., and if one ignores the lowest temperature run it is borne out in the data of Keyser as well.

In summary, it is now well established that earlier measurements underestimated the rate constant for the OH + H_2O_2 reaction by about a factor of two for reasons that have been discussed elsewhere at length (Sridharan et al., 1982; Kurylo et al., 1982). The results of the most recent flash photolysis and discharge flow studies are in very good agreement with each other, except possibly at 250 K and below, where our numbers show an increase in the rate constant with decreasing temperatures, indicating the formation of an intermediate hydrogen-bonded addition complex.

Table 2. Comparison of Recent Rate Measurements for the OH + H_2O_2 Reaction

Temperature (K)	(a)	(b)	k_1 $(10^{-12}cm^3molecule^{-1}s^{-1})$* (c)	(d)	(e)**
241	1.50 ± 0.30	1.49 ± 0.48	1.26 ± 0.29	1.49 ± 0.31	2.04 ± 0.51
251	1.54 ± 0.30	1.52 ± 0.39	1.31 ± 0.28	1.53 ± 0.31	1.97 ± 0.46
294	1.69 ± 0.26	1.64 ± 0.32	1.53 ± 0.28	1.68 ± 0.30	1.79 ± 0.30
333	1.85 ± 0.32	1.72 ± 0.36	1.69 ± 0.34	1.79 ± 0.34	1.75 ± 0.35
365	1.89 ± 0.36	1.78 ± 0.45	1.81 ± 0.40	1.87 ± 0.38	1.77 ± 0.41
413	1.99 ± 0.42	1.85 ± 0.52	1.97 ± 0.47	1.97 ± 0.42	1.85 ± 0.49

(a) Sridharan et al. (1980).

(b) Keyser (1980).

(c) Wine et al. (1982).

(d) Kurylo et al. (1982).

(e) This work.

* Computed from the Arrhenius expression and error bars given by each group. The error bars for $T \neq 294$ K were estimated as explained by the NASA Panel for Data Evaluation (DeMore et al., 1982).

** Computed from Equation 6, with an error bar at 294 K of $\pm$ 0.3 x 10^{-12}, and error bars at other temperatures as above.

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